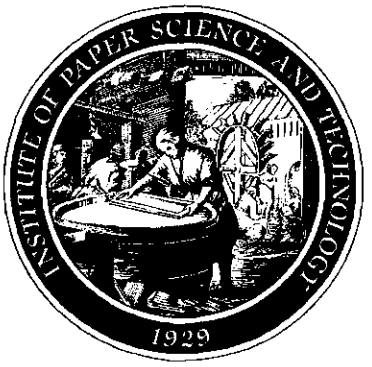

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On the Improved Selectivity of Oxygen Delignification
1. Fiber Curl, Crystallinity and Length

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ON THE IMPROVED SELECTIVITY OF OXYGEN DELIGNIFICATION. 1. FIBER CURL, CRYSTALLINITY AND LENGTH

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ABSTRACT

The purpose of this research was to gain a better understanding of the phenomena affecting fiber quality in oxygen delignification. Softwood kraft pulps were oxygen delignified to six different extents using different temperatures and alkali charges as variables in a factorial experiment. Each of the oxygen-delignified pulp samples, as well as two brownstock samples, was subjected to conventional DEDED bleaching at a constant first-stage kappa factor. The fully bleached samples were then characterized in terms of fiber length and curl by image analysis and amorphous/crystalline cellulose ratio by CP/MAS ^{13}C-NMR.

INTRODUCTION

Pulps that have been oxygen delignified to an extent of 50% or less generally exhibit a tear factor at a given tensile strength that is similar to that of conventionally bleached pulps, despite having a lower viscosity [1]. However, it is well established that intensive oxygen delignification, e.g., two-stage oxygen treatment prior to nonchlorine chemical bleaching, tends to be non-selective. Under these conditions, there may be significant effects on fiber properties. For example, cellulose crystallinity may be affected, fiber curl may be introduced, or the ability of the fibers to form bonds with other fibers may be compromised. Furthermore, fiber strength may be affected. The resulting reductions in pulp quality become evident when the pulps are compared to pulps prepared by conventional chlorine dioxide bleaching, which is known to be very selective.

The purpose of this research was to gain a better understanding of the phenomena affecting fiber quality in oxygen delignification.

EXPERIMENTAL

The pulp sample (softwood kraft) was obtained from a Finnish mill. The properties of the pulp sample were as follows: kappa number 25.6, viscosity 1244 mL/g, and brightness 27.3% ISO.

The softwood pulps were oxygen delignified to six different extents of delignification by using temperature and alkali charge as variables. All combinations of the following temperatures and alkali charges were included in the experiments: 80°C and 95°C; 1%, 2%, and 4% NaOH. Oxygen delignification was performed in a Quantum mixer at 10% consistency and 90 psi pressure. No magnesium salt was used.

Each of these oxygen-delignified pulp samples as well as two reference brownstock samples underwent a conventional chlorine dioxide (ECF) bleaching in the DEDED sequence. Chemical charges in the bleaching stages varied and depended on the post-oxygen kappa number (constant kappa factor 0.2 in D_0). Otherwise, the conditions were the same for all pulps. All D and E bleaching stages were carried out in a water bath except the D_0 stage for the Reference 2 pulp sample, which was performed in a Quantum mixer. A Hobart mixer was used for pulp homogenizations between the bleaching stages. The target brightness after bleaching was 88+. The brownstock and fully bleached samples as well as a fully bleached mill pulp sample (10 samples in all) were then characterized.

ANALYSES

Brightness, kappa number, and viscosity were determined according to ISO 2469:1994(E), TAPPI T236 cm-85, and SCAN-CM 15:88, respectively.

The pulp samples were analyzed with an Optest Fiber Quality Analyzer (FQA) for fiber length and curl, both length-weighted averages.

The pulp samples were Wiley milled using a screen with 0.050" diameter holes. The samples were then analyzed with Cross Polarization Magic Angle Spinning Carbon-13 Nuclear Magnetic Resonance Spectroscopy (CP/MAS ^{13}C-NMR) for amorphous and crystalline cellulose. The measurements were carried out with a Bruker 400 MHz DMX Spectrometer. Similar methods have been described elsewhere [2-4].

RESULTS AND DISCUSSION

The effect of sodium hydroxide charge and temperature on kappa number in oxygen delignification is presented in Figure 1.

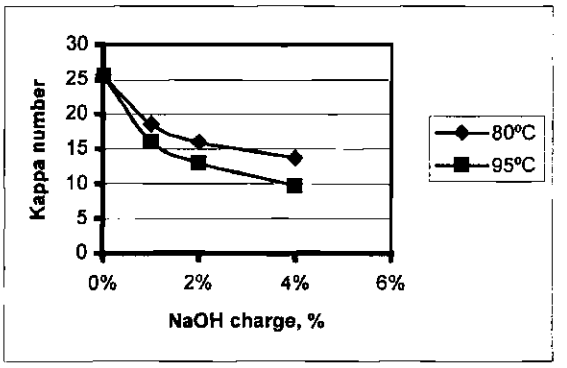

Figure 1. The effect of NaOH dose and temperature on kappa number in oxygen delignification.

As can be seen in Figure 1, the highest sodium hydroxide charge (4%) and temperature (95°C) resulted in a relatively high delignification rate, about 62%. The lowest NaOH charge (1%) and 80°C temperature only

decreased kappa number by some 27%. The effect of sodium hydroxide charge and temperature on selectivity (viscosity as a function of kappa number) in oxygen delignification is presented in Figure 2.

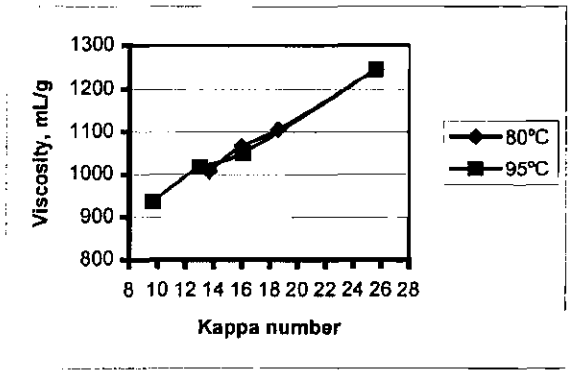

Figure 2. The effect of temperature and NaOH dose on selectivity in oxygen delignification.

As Figure 2 illustrates, the change in viscosity as a function of kappa number decrease was quite linear. In fact, the specific viscosity drop was between 18 and 20 mL/g for all pulp samples.

After oxygen delignification, all eight oxygen-delignified pulp samples as well as two reference brownstock samples were bleached in a DEDED sequence. The most important findings of the bleaching experiments are presented in Table 1.

Table 1. DEDED or ODEDED bleaching results.

DEDED or ODEDED bleaching treatment	Total ClO_2 %	Bright, % ISO	Visco, mL/g
No O_2, D_0 in water bath	4.35	89.0	908
No O_2, D_0 in Quantum	3.45	88.5	1040
95°C & 4% NaOH in O_2	1.70	89.4	863
95°C & 2% NaOH in O_2	2.20	89.0	939
95°C & 1% NaOH in O_2	2.60	89.1	943
80°C & 4% NaOH in O_2	2.25	89.9	920
80°C & 2% NaOH in O_2	2.60	88.9	957
80°C & 1% NaOH in O_2	3.20	89.6	879
Oxygen-ECF mill pulp	n/a	86.5	975

As can be seen in Table 1, the use of a Quantum mixer in the D_0 stage greatly increased the efficiency of chlorine dioxide delignification and therefore decreased the need for chlorine dioxide in the following D stages. As a result of this, the final viscosity also remained on a substantially higher level. The large beneficial effect of good mixing in the D_0 stage resulted, in part, from the fact that this particular pulp had not been subjected to oxygen delignification in the Quantum mixer. Prior treatment in the Quantum mixer facilitated mixing in subsequent stages.

The final brightnesses demonstrate that the use of oxygen delignification is an efficient means of reducing the kappa number and therefore decreasing the use of chlorine dioxide. The pulps that had been treated with an O_2 stage did not, on average, suffer a viscosity drop any greater than the DEDED reference pulp bleached in a water bath. The reference ECF mill pulp also had relatively high viscosity. The brightness of the mill pulp sample had ebbed a couple of ISO brightness units after being shipped from the mill, apparently due to ordinary brightness reversion. Other bleaching results are presented in the Appendix.

The FQA results are presented in Table 2.

Table 2. FQA results after bleaching.

DEDED or ODEDED bleaching treatment	Fiber length (l/w), mm	Curl (l/w)
No O_2, D_0 in water bath	2.23	0.276
No O_2, D_0 in Quantum	2.18	0.318
95°C & 4% NaOH in O_2	2.09	0.335
95°C & 2% NaOH in O_2	2.12	0.345
95°C & 1% NaOH in O_2	2.09	0.344
80°C & 4% NaOH in O_2	2.14	0.338
80°C & 2% NaOH in O_2	2.11	0.337
80°C & 1% NaOH in O_2	2.19	0.321
Oxygen-ECF mill pulp	2.17	0.250

As Table 2 shows, fiber length apparently underwent a slight decrease as a result of oxygen delignification, while curl increased. The fiber length of the reference mill pulp equaled those of the mildly treated oxygen-delignified laboratory pulps. The more severe the oxygen treatment, the greater was the introduction of curl and the greater the apparent decrease in fiber length. It is likely that the apparent fiber length decrease is an artifact of the measurement method, inasmuch as curled fibers that are not aligned within the plane of measurement will project an apparent length that is less than their true length. The laboratory mixers, both Quantum and Hobart, probably introduced most of this fiber curl.

The CP/MAS ^{13}C-NMR spectrum of an extensively oxygen-delignified (95°C and 2% NaOH) and bleached kraft pulp sample is shown in Figure 3.

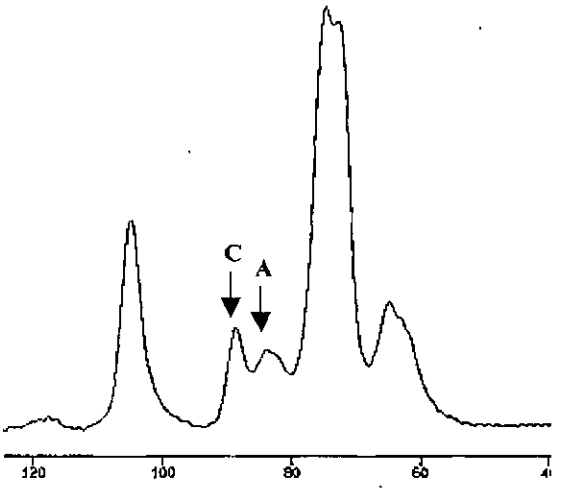

Figure 3. CP/MAS ^{13}C-NMR spectrum of fully bleached kraft pulp. A and C denote amorphous and crystalline cellulose, respectively.

As can be seen in Figure 3, the spectrum shows signals of crystalline and amorphous celluloses and can therefore be used to determine the ratios of the contents of these celluloses [2-4]. When the spectra of this study were observed visually, little or no difference could be seen. The calculated results obtained from CP/MAS ^{13}C-NMR spectra of the fully bleached samples are presented in Table 3.

Table 3. Solid-state ^{13}C-NMR spectroscopy results.

O_2 treatment of the fully bleached sample	Amorphous cellulose/ crystalline cellulose ratio
No O_2, D_0 in water bath	1.05
No O_2, D_0 in Quantum	1.04
95°C & 4% NaOH in O_2	1.03
95°C & 2% NaOH in O_2	1.03
95°C & 1% NaOH in O_2	1.04
80°C & 4% NaOH in O_2	1.03
80°C & 2% NaOH in O_2	1.06
80°C & 1% NaOH in O_2	1.04
Oxygen-ECF mill pulp	1.00

As can be seen in Table 3, the amorphous/crystalline cellulose ratios are virtually the same for all laboratory pulp samples. The amorphous/crystalline cellulose ratio of the brownstock was 1.04. Therefore, the ratio did not change as a result of laboratory bleaching. The mill reference pulp, however, shows a slightly lower amorphous/crystalline cellulose ratio, which is probably due to the more severe treatment in mill conditions.

CONCLUSIONS

According to the results, the Scandinavian softwood used in these experiments was resistant to viscosity loss during oxygen delignification. The use of extensive oxygen delignification did, however, introduce a considerable fiber curl, which was accompanied by an apparent slight decrease in fiber length. The mixing devices used in the laboratory were probably responsible for the introduction of curl.

Results obtained from CP/MAS ^{13}C-NMR spectra showed no differences among the laboratory pulps in terms of the amorphous/crystalline cellulose ratio. Even the pulp samples that had experienced extensive oxygen delignification had virtually the same amorphous/crystalline cellulose ratio as that of the brownstock pulp. The amorphous/crystalline cellulose ratio of the mill reference pulp was slightly lower than those of the laboratory pulps, which is obviously due to the more severe treatments in the mill.

ACKNOWLEDGMENTS

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APPENDIX

Table 4. Oxygen delignification results.

DEDED or ODEDED bleaching treatment	Kappa number	Brightness, % ISO	Viscosity, mL/g	Specific viscosity drop, mL/g
95°C & 4% NaOH in O_2	9.7	42.3	936	19
95°C & 2% NaOH in O_2	13.0	35.3	1017	18
95°C & 1% NaOH in O_2	16.1	31.3	1050	20
80°C & 4% NaOH in O_2	13.7	34.9	1007	20
80°C & 2% NaOH in O_2	16.0	31.8	1067	18
80°C & 1% NaOH in O_2	18.6	29.3	1105	20

Table 5. Bleaching results after the initial bleaching stages, ODED

DEDED or ODEDED bleaching treatment	ClO_2 in D_0, %	NaOH in E_1, %	ClO_2 in D_1, %	Brightness, % ISO	Viscosity, mL/g
No O_2, D_0 in water bath	1.95	2.6	1.2	69.0	1102
No O_2, D_0 in Quantum	1.95	2.6	1.2	80.4	1083
95°C & 4% NaOH in O_2	0.75	1.1	0.75	81.9	871
95°C & 2% NaOH in O_2	1.0	1.4	0.9	79.9	963
95°C & 1% NaOH in O_2	1.2	1.7	1.0	78.6	1001
80°C & 4% NaOH in O_2	1.05	1.4	0.9	80.4	955
80°C & 2% NaOH in O_2	1.2	1.7	1.0	79.4	1008
80°C & 1% NaOH in O_2	1.4	2.0	1.1	75.9	1034

Table 6. Chemical charges in the E_2 and D_2 stages.

DEDED or ODEDED bleaching treatment	NaOH in E_2, %	ClO_2 in D_2, %
No O_2, D_0 in water bath	0.7	1.2
No O_2, D_0 in Quantum	0.7	0.3
95°C & 4% NaOH in O_2	0.7	0.2
95°C & 2% NaOH in O_2	0.7	0.3
95°C & 1% NaOH in O_2	0.7	0.4
80°C & 4% NaOH in O_2	0.7	0.3
80°C & 2% NaOH in O_2	0.7	0.4
80°C & 1% NaOH in O_2	0.7	0.7